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OCCURRENCE, DISTRIBUTION, AND SIGNIFICANCE OF ALKALI CYANIDES IN THE IRON BLAST FURNACE

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OCCURRENCE, DISTRIBUTION, AND SIGNIFICANCE OF ALKALI CYANIDES IN THE IRON BLAST FURNACE[1]

By S. P. KINNEY and E. W. GUERNSEY[2]

INTRODUCTION

For a number of years the Bureau of Mines has been studying the physical and chemical reactions that take place during the smelting of iron in the blast furnace. It has made experiments in the laboratories of the experiment stations at Pittsburgh, Pa., and Minneapolis, Minn., has made test runs with an experimental blast furnace at Minneapolis, and has collected a large mass of data on the work done by commercial blast furnaces. This paper describes an investigation made in the course of the broader studies.

The presence of alkali cyanides in the interior of the iron blast-furnace has been noted repeatedly during a period of almost 100 years, and has been studied more or less closely by a few persons. Reliable information on the concentration of cyanides at various points inside of present-day blast furnaces is necessary in order to determine the desirability of attempting to recover the cyanides as a by-product. Furthermore, many persons have thought the cyanides have important effects on the production of iron by the furnace. Bunsen in 1845 and Lowthian Bell in 1872 made some quantitative measurements of the concentration of cyanides in the blast furnace, but their results were not consistent enough to provide a safe basis for calculation. Their method of making the measurements is also open to question, as will be seen later.

In order to establish more definitely the alkali-cyanide concentration in the gases from various regions of the modern blast furnace, the authors of this paper undertook an investigation in 1924 in conjunction with a more general study of the fundamental reactions occurring in the blast furnace. In the course of that study, samples of gas and stock were taken across a series of planes at various heights in the furnace.

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[1] A joint study by the Bureau of Mines, the fixed-nitrogen research laboratory of the Department of Agriculture, and the Central Iron & Coke Co., Holt, Ala.

[2] Kinney, S. P., and Guernsey, E. W., "The occurrence of alkali cyanides in the iron blast furnace": Ind. and Eng. Chem., vol. 17, July, 1925, pp. 670–674.

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The intention is to extend this investigation ultimately to several blast furnaces in order to note the variations in cyanide concentration with variations in charge and operating conditions. The measurements for one furnace have been completed. The present paper gives the results and a résumé of previous work bearing on the subject.

The furnace studied belongs to the Central Iron & Coal Co., at Holt, Ala., and produces about 290 tons of foundry iron a day. The authors gratefully acknowledge the courtesy of officials of that company, particularly Fraser B. McKenzie, blast-furnace superintendent, and J. L. Brierton, vice president and general manager, in providing the opportunity for making this study.

QUANTITY OF ALKALI CYANIDES FORMED IN AMERICAN BLAST FURNACES

The following estimate of the maximum possible formation of cyanides in American blast furnaces should enable the reader to form an opinion as to the extent to which cyanides recovered from blast furnaces might be expected to supply domestic demands, either for cyanides or for ammonia and other fixed nitrogen products obtainable from cyanides. The maximum amount of cyanides that might be recovered is fixed by the quantity of alkali (Na_2O and K_2O) contained in the raw materials fed to the furnaces. At present reliable data are available only on the quantity of K_2O in these materials. According to a survey made by the Bureau of Soils,[3] the total potash, K_2O, entering the blast furnace is about 222,900 tons a year, if the average metal production and consumption of raw materials from 1913 to 1920 be taken as the basis of computation. This total is equivalent to 308,000 tons of KCN or 60,000 tons of nitrogen a year.

Little information is available on the Na_2O content of the blast-furnace charge. The proportion is generally too small to take into account in ordinary calculations of blast-furnace burdening, and hence is seldom determined. In the few available ore analyses that include an alkali determination, and in analyses of the rocks associated with the ore, the general tendency is for the content of K_2O to exceed considerably that of Na_2O. Hence it is probably safe to assume that the maximum formation of cyanide will not be more than 50 per cent greater than that calculated on the basis of K_2O alone, making this maximum equivalent to 460,000 tons of KCN or 90,000 tons of fixed nitrogen a year. The actual recovery of KCN in practice will, of course, be much less, for two reasons: (1) It will not be possible to recover in combination with nitrogen all of the alkali passing into a given furnace, and (2) at many furnaces the alkali content of the charge may be too low to justify recovery. The work described in this paper will give an approximate idea of the proportion of the total alkali that may be expected to be recoverable as cyanide. The figures above, however, show that the amounts of fixed nitrogen which might be regarded as recoverable are small in comparison with the total inorganic nitrogen requirement of the country, which is about 200,000 tons of nitrogen a year. On the other hand, even a fraction of the alkali passing into our blast furnaces will suffice to supply the total requirement for cyanides, which, calculated as NaCN, is perhaps 20,000 tons a year.

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[3] Merz, A. B., and Ross, W. H., Recovery of Potash as a By-Product in the Blast-Furnace Industry: Bull. 1226, Department of Agriculture, 1924, 22 pp.

ACCUMULATION AND CIRCULATION OF CYANIDES AND OTHER ALKALI COMPOUNDS IN THE BLAST FURNACE

In the ore, limestone, and coke of the blast-furnace charge the alkaline oxides are combined as complex silicates, and constitute about 0.2 to 0.5 per cent of the total charge. As these silicates move through the bosh and hearth of the furnace where the temperature is very high, 900° to 1,500° C., a part of the alkali oxide is displaced by lime—

$$K_2SiO_3 + CaO = CaSiO_3 + K_2O. \qquad (1)$$

This alkali oxide is converted to cyanide,

$$K_2O + N_2 + 3C = 2KCN + CO. \qquad (2)$$

At the temperature existing the cyanide formed must be entirely in the gas phase, and so joins the upward-moving gas. Very little of the cyanide, however, reaches the top of the furnace; part of it condenses in the charge in the cooler part of the stack and part reacts with the charge and with the CO_2 and CO of the gases to form alkali silicate and carbonate, which are carried down with the charge and cyanide is again formed as before. In this way the concentration of the cyanides in the gas and the alkali constituents in the charge builds up until a balance is reached, such that the amount of alkali passing out of the furnace in the top gases and in the slag is just equal to that being supplied by the raw materials. In this way noteworthy concentrations may build up in the furnace, even through the amount of alkali in the charge is comparatively small.

PREVIOUS INVESTIGATIONS

WORK OF DAWES, CLARK, ZINKEN AND BROMEIS, AND REDTENBACHER

The first definite record of the detection of cyanides in the blast furnace is contained in a British patent to John Dawes,[4] of the Bramford Iron Works. In this patent he claimed a means of collecting

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[4] British patent No. 6048, 1835.

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KCN by inserting an iron pipe into the furnace wall near the tuyères. In 1837 Clark[5] analyzed some sublimate that collected around the bosh in a blast furnace and found considerable quantities of cyanide. In 1841 Zinken and Bromeis[6] noticed that charcoal remaining in the bottom of a blown-out furnace was impregnated with saline matter which contained KOH, K_2CO_3, K_2SiO_3, KCNO, KCN, and $K_4Fe(CN)_6$.

In 1843 Redtenbacher[7] published an account of the formation of considerable quantities of cyanide at the Mariazell iron furnace in Styria. At this furnace gas was allowed to escape through a small hole in the bosh and burn at night for illumination. A fused material—largely KCN and K_2CO_3—collected around the hole. Numerous other writers have qualitatively confirmed the presence of KCN in the interior of the blast furnace and in incrustations at various points about the furnace.

QUANTITATIVE WORK OF BUNSEN AND PLAYFAIR

The first quantitative measurements of the amount of cyanides in the gas inside the furnace were reported by Bunsen and Playfair[8] in 1845. They drilled a hole in the bosh of the furnace at Alfreton, England, at a point 33 inches above the tuyères, inserted an iron pipe into the hole, but only part way through the wall, and by bubbling it through water absorbed the fume which was blown out. The amount of KCN found, including both that which settled in the pipe and that absorbed, was about 8 or 10 ounces per 1,000 cubic feet.

QUANTITATIVE WORK OF BELL

Lowthian Bell attempted to determine more definitely the zone of formation of the cyanides in the furnace by drilling a series of holes through the wall of the furnace at different heights and examining the gases which issued at the different levels. He made such examinations on several occasions and at least at two different furnaces. Table 1 is compiled from data by Bell[9] obtained at a furnace at Wear, England. This furnace had a capacity of 17,500 cubic feet, was 80 feet high, and had a bosh diameter of 20.5 feet.

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[5] Clark, Thomas, "Cyankalium, ein zufalliges Product bei der Bereitung des Gusseisens in Hohofen": Ann. Physik und Chemie, Bd. 40, 1837, pp. 315–318.

[6] Zinken, O., and Bromeis, "Ueber die Bildung von Cyanverbindungen in den Producten des Magdesprunger Hohofens"; Jour. prakt. Chemie, Bd. 25, 1842, pp. 246–253.

[7] Redtenbacher, Jos., "Schwarzes und weisses Salz des Hohofens von Mariazell in Steiermark": Ann. Chem. und Pharm., Bd. 47, 1843, pp. 150–153.

[8] Bunsen R. W., and Playfair, L., "Report on the gases evolved from iron furnaces with reference to the theory of smelting of iron": Brit. Assoc. Rept., 1845, pp. 142–146; Jour. Pharm., t. 14, 1848, pp. 441–444.

[9] Bell, I. Lowthian, Chemical Phenomena of Iron Smelting. London, 1872, p. 136.

TABLE 1.—*Cyanides and alkali at various heights in a furnace at Wear, England, according to Bell*

Height above tuyères, feet	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
8	122.0	233.0	52.4
24	39.3	44.5	88.4
60	19.1	62.6	30.5
76	14.8	49.3	30.0
80 (top gases)	11.8	10.7	110.0

The figures for the gases taken 8 feet above the tuyères seem high, because in repeated experiments at this point and in tests of the top gases Bell obtained the results shown in Table 2.

TABLE 2.—*Cyanides and alkali at 8 feet above the tuyères and in escaping gases of the furnace at Wear, England*

Source of gas	Alkali and cyanides							
8 feet above tuyères	Total alkali, calculated as KCN	82.2	54.4	60.1	38.3	58.5	25.9	52.9
	Cyanide, calculated as KCN	47.5	32.4	43.4	28.4	51.6	22.9	37.7
	Alkali as cyanide, per cent	58.0	50.0	72.0	74.0	88.0	88.0	71.0
In escaping gases	Total alkali, calculated as KCN	-------	20.7	29.3	15.5	11.4	10.3	17.4
	Cyanide, calculated as KCN	-------	10.0	16.5	8.9	7.3	4.5	9.4
	Alkali as cyanide, per cent	-------	48.0	56.0	57.0	64.0	44.0	54.0

The reader will note that at 8 feet above the tuyères the average concentration of KCN is 37.7 ounces per 1,000 cubic feet, as compared with 122 ounces per 1,000 cubic feet found in the experiments of Table 1. Later experiments by Bell on a furnace at Clarence, England, gave the results in Table 3.[10] The furnace was 80 feet high and had a capacity of 25,500 cubic feet.

TABLE 3.—*Cyanides and alkali at various heights in a furnace at Clarence, England, according to Bell*

Height above tuyères, feet	Number of experiments averaged	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Total alkali,[a] ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
8	6	62.8	80.7	78
21.5	1	65.8	88.7	74
50.5	1	32.0	71.7	45
60	1	24.8	67.1	37
Escaping gases	5	15.8	25.1	63

[a] Reported by Bell in terms of Na+K, but assumed in this calculation as all K.

[10] Bell, I. Lowthian, Principles of the Manufacture of Iron and Steel. London, 1884, p. 218.

Other experiments on the same furnace indicated a much lower concentration of alkaline salts in the gases. Table 4 shows concentrations only one-tenth of the corresponding values in Table 3.

TABLE 4.—*Cyanides and alkali in a furnace at Clarence, England, according to Bell*

Height above tuyères, feet	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
2	10.35	14.27	72.5
26.5	7.28	7.62	95.5
39.75	1.61	1.71	94.2
76 (escaping gases)	0	.047	0

RECENT PATENTS FOR RECOVERY OF CYANIDES

Since Bell made his experiments, about 1870, no extensive measurements have been published, as far as the authors are aware, on the quantity of alkaline cyanides in the blast furnace. There is, however, no lack of interest on the subject, as is evidenced by the number of patents issued in recent years on the recovery of cyanides as a blast furnace by-product and on the use of modified blast furnaces for the primary production of cyanides or for producing ammonia through cyanides as an intermediate step. The patents of Craig,[11] Weaver and Gayley,[12] and McElroy [13] have to do primarily with the recovery of cyanides from blast furnaces operated in the usual manner for the production of iron. The patent of Addie, Cunningham, and McFarlane,[14] and those of Sieperman,[15] Haslup,[16] McElroy,[17] Spencer and McElroy,[18] and Meadows [19] contemplate making alkali cyanides and other nitrogen compounds as main products in internally fired furnaces patterned more or less after the conventional design of the iron blast furnace.

WORK OF FRANCHOT

One of the more recent contributions to the literature on cyanides in the blast furnace is by Franchot,[20] who stresses particularly the

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[11] United States Patent No. 600137, 1898.

[12] United States Patent No. 1322038, 1919.

[13] United States Patent No. 1466624 and 1466625, 1923.

[14] British Patent No. 12572, 1893.

[15] British Patent No. 13754, 1893.

[16] United States Patents No. 1310478, 1310479 and 1310480, 1919.

[17] United States Patents No. 1390533 and 1466626, 1919.

[18] United States Patent No. 1156108, 1915.

[19] United States Patent No. 1292937, 1919.

[20] Franchot, Richard, "Fixation of nitrogen as cyanide": Jour. Ind. and Eng. Chem., vol. 16, 1924, pp. 235–238. Economic Significance of Cyanide Accumulation in the Blast Furnace: Preprint 1470–C, Am. Inst. Min. and Met. Eng., July, 1925.

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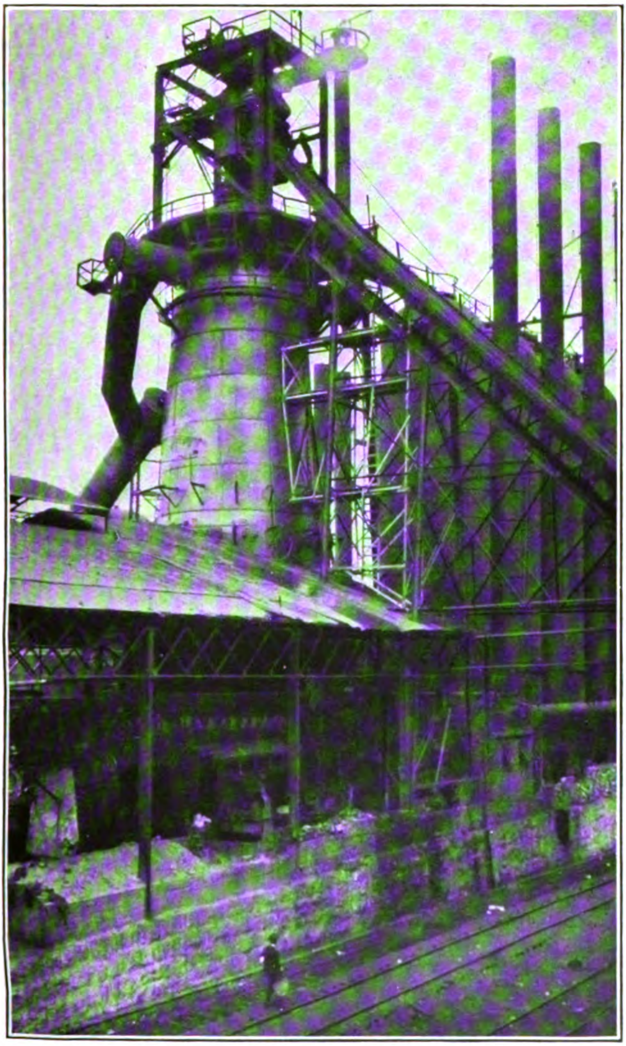

FIG. 1.—General view of 300-ton furnace where investigation was made

adverse effect on the fuel economy of the furnace from the formation in the hearth and the distillation therefrom of large quantities of alkali cyanide.

EXPERIMENTAL WORK BY KINNEY AND GUERNSEY

Figure 1 gives a general view of the 300-ton blast-furnace plant where the authors of this paper made their investigation.

Under the skip hoist may be seen the temporary platforms used in taking samples through the furnace wall at various heights. In the foreground is the cast house. The slag notch is on the side opposite to the skip hoist.

ANALYSES OF CHARGE MATERIALS, SLAG, AND FLUE DUST

Table 5 gives analyses of some typical iron ores of the Alabama district where this furnace is situated. The analyses are in somewhat greater detail than may seem necessary for the present purpose, but they are given because few detailed analyses of these ores have appeared in the literature. Red ores are used for about 70 per cent of the production, and of these shown the Attala ore is the most important. Of the brown ores, the Shelby and Friedman are the most largely used.

TABLE 5.—*Analyses of typical southern ores*

	Red (hematite) ores			Brown ores			
	Attala[1]	Valley View	Sloss	Shelby	Janifer	Fried-man	Opelika
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Moisture	0.3	0.2	0.3	2.0	1.0	3.5	1.2
Silica (SiO_2)	9.9	24.8	10.9	9.3	9.6	13.1	10.9
Alumina (Al_2O_3)	5.4	3.1	3.6	5.1	2.7	5.2	5.3
Ferric oxide (Fe_2O_3)	57.4	53.5	55.1	73.6	73.0	63.2	68.2
Manganous oxide (MnO)	.12	.11	.19	1.23	.21	.58	.10
Phosphorus oxide (P_2O_5)	.31	.33	.42	.31	2.20	1.56	2.98
Lime (CaO)	12.40	9.20	15.0	0	0	.2	.2
Magnesia (MgO)	1.50	.4	.3	.1	.1	.2	0
Soda (Na_2O)	0	.1	.7	.1	.3	.3	0
Potash (K_2O)	.8	.4	.4	.1	.3	.3	.2
Sulphur (S)	.1	0	0	0	0	.1	0
Carbon dioxide (CO_2)	10.7	6.8	12.1	.2	.2	.8	.1
Loss on ignition[2]	.9	.8	1.0	8.0	10.7	10.9	10.5
Total	99.83	99.74	100.01	100.04	100.31	99.94	99.68

[1] Composite sample of 36 cars.

[2] Less moisture and CO_2.

As the table shows, the alkali oxide content of the ores varies widely. The percentage of Na_2O exceeds that of K_2O in only one analysis. The charge for this furnace was composed of a mixture of red and brown ore in varying proportion and from nodules made from pyrite sinter. Detailed analyses were made on composite samples of each of these ores and on the limestone and coke used. From these analyses and from the relative amounts used the average composition of the charge is calculated; it is shown in Table 6, together with analyses of composite samples of the slag, flue dust, and stove dust. The analyses correspond to a period of furnace operation that does not coincide exactly with the period during which the cyanide determinations were made.

TABLE 6.—*Composition of furnace charge and products*

	Charge	Slag	Flue dust	Stove dust
	Per cent	*Per cent*	*Per cent*	*Per cent*
Moisture (H_2O)	7.44		0.30	0.01
Silica (SiO_2)	8.31	32.15	12.9	
Alumina (Al_2O_3)	3.81	16.23	7.1	
Iron (Fe)	3.91			
Ferrous oxide (FeO)	2.46			
Ferric oxide (Fe_2O_3)	28.35	0.41	49.0	
Lime (CaO)	6.94	32.29	5.2	
Magnesia (MgO)	3.31	15.88	1.6	
Phosphoric oxide (P_2O_5)	.46	.33	.35	
Manganous oxide (MnO)	.29	.21	.49	
Potash (K_2O)	.26	.64	1.20	7.9
Soda (Na_2O)	.17	.45	1.43	.8
Sulphur (S)	.40	1.41	.30	
Carbon dioxide (CO_2)	8.86		5.06	
Carbon (C)	25.02		15.07	
Total water-soluble				9.0
Total	99.99	100.00	100.00	
Pounds per long ton of metal produced	8,426	1,786	279	29

As the table shows, the charge contained an average of 0.28 per cent K_2O and 0.18 per cent Na_2O, the total equivalent to 0.55 per cent K_2O. The weighted average content of K_2O for all blast-furnace charges in the United States is, according to the Bureau of Soils survey already mentioned,[21] about 0.2 per cent. From the figures in the table it is calculated that the total alkali oxide charged is equivalent to 43.5 pounds of K_2O per ton of metal produced. The alkali discharged in slag, flue dust, and stove dust, calculated from the analyses and quantities of these materials, is only 35.6 pounds calculated as K_2O. The remaining 7.9 pounds of alkali could be completely accounted for if the wash water from the gas scrubber should be found to contain 0.0916 ounce of alkali (calculated as K_2O) per gallon (400,000 gallons of water a day being assumed). As an average of 0.035 ounce of KCN was found in the water (unfortunately the total alkalinity was not determined), it seems probable that the total alkali was sufficient to account completely for the discrepancy. As Table 7 shows, determinations of cyanides in wash water were variable; the amounts were much larger after a slip in the furnace than during smooth operation.

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[21] Merz, A. R., and Ross, W. H., work cited. See footnote 2.

TABLE 7.—*Cyanides in water* [1] *from the gas washers*

Experiment No.	Cyanide per gallon, calculated as KCN, ounce	Cyanide concentration, ounce per 1,000 cubic feet	Remarks	Experiment No.	Cyanide per gallon, calculated as KCN, ounce	Cyanide concentration, ounce per 1,000 cubic feet	Remarks
1	0.0563	0.41	Blast off.	6	0.0092	0.067	
2	.0268	.20	Operation normal.	7	.0028	.021	Before a furnace slip.
3	.0929	.68	After a furnace slip.	8	.0134	.098	After a furnace slip.
4	.0158	.12		9	.0239	.17	Do.
5	.0134	.098		10	.0936	.68	Cleaning out gas washer.

[1] Volume of wash water assumed to be 400,000 gallons a day.

If it is assumed that the 7.9 pounds of alkali per ton of metal not quantitatively accounted for is removed by the wash water, then of the 43.5 pounds of alkali oxide charged 23.6 pounds, or 54 per cent of the total, passed out of the furnace in the slag and the remaining 46 per cent in the top gases. The Bureau of Soils survey indicated that for all the furnaces of the country 37.5 per cent of the K_2O charged is volatilized from the top.

It is further calculated from the slag analysis given in Table 6 that the weight ratio of base (CaO, MgO) to acid (SiO_2, Al_2O_3) is about 0.993. This ratio is of interest, because the extent to which alkali oxide is displaced by lime in the furnace depends somewhat on the basicity of the slag. Stoughton [22] quotes analyses of slags from 26 modern blast furnaces running on Lake Superior, Spanish, and Cuban ores. The base-acid ratio $(CaO+MgO) \div (SiO_2+Al_2O_3)$ calculated from these analyses ranged from 0.95 to 1.42, with an average value of 1.15. The average for 11 furnaces using Lake Superior ore with Connellsville coke and part anthracite coal was 1.05. Analyses given by Bell [23] of slags produced about the year 1870 indicate that in general the slags then were more acid; the base-acid ratio of 8 slags mentioned ranged from 0.71 to 0.94, with an average value of 0.80. The base-acid ratio given by Royster, Joseph, and Kinney for 14 northern blast furnaces was 0.967.[24]

CONCENTRATION OF ALKALI CYANIDES AND OTHER ALKALINE COMPOUNDS IN THE GASES WITHIN THE FURNACE

COLLECTION OF GAS

The gas-sampling holes in the wall of the furnace were 2½ inches in diameter and were drilled as shown in Figure 2. A nipple and gate valve attached to the shell provided an entrance to the furnace.

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[22] Stoughton, Bradley, Metallurgy of Iron and Steel. 3d ed., New York, 1923, p. 31.

[23] Bell, I. Lowthian, Chemical Phenomena of Iron Smelting. London, 1872, pp. 138 and 270. Principles of the Manufacture of Iron and Steel. 1884, pp. 392 and 394.

[24] Royster, P. H., Joseph, T. L., and Kinney, S. P., "Heat balance of Bureau of Mines experimental furnace": Blast Furnace and Steel Plant, vol. 12, p. 200-204.

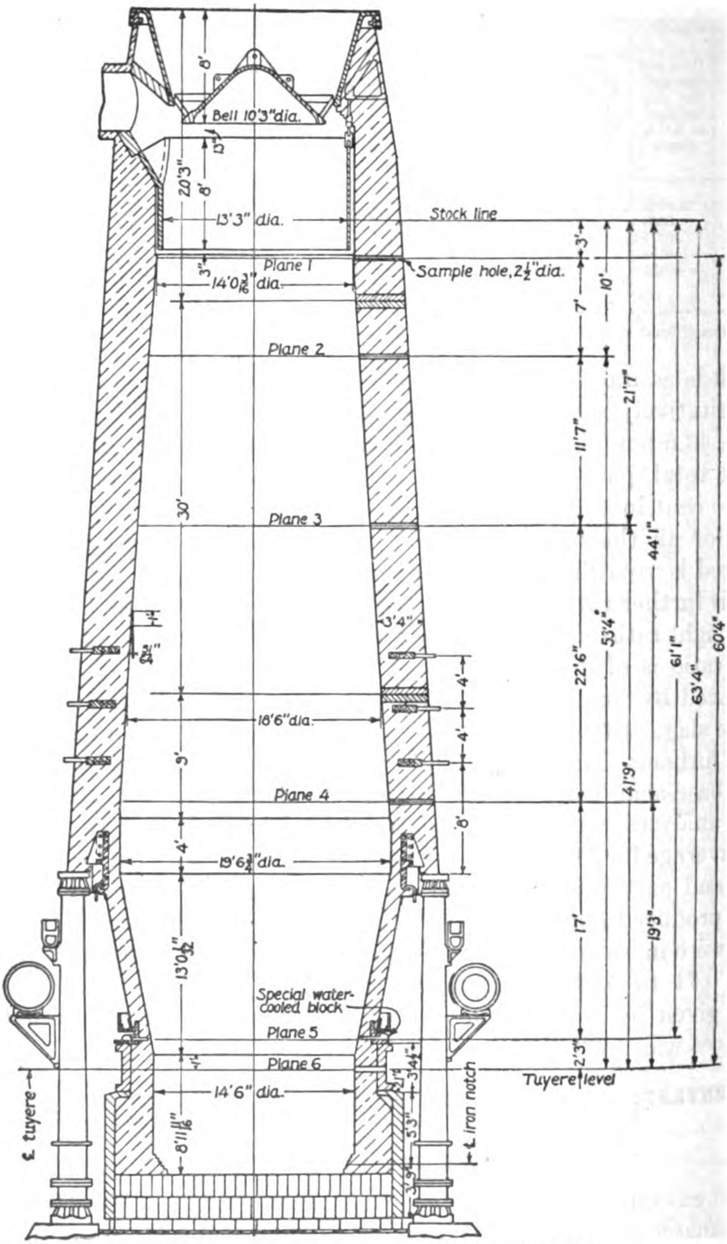

Figure 2.—Section of furnace, showing sampling holes

The water-cooled sampling tube used for withdrawing samples for gas analysis and cyanide determination was designed by Perrott and Kinney for use in earlier work on the composition of the blast-furnace gases, and has been described in detail elsewhere.[25] The tube was 2 inches outside diameter and the inside gas passage was ⅜ inch. Tubes of various lengths were used, but the standard length was 17 feet.

In obtaining samples of gas the sample tube was driven to the center of the furnace with a dolly bar; the tube had a shoulder welded on it for this purpose. During the insertion of the tube the gas passage was kept free of slag, coke, etc., which might have tended to plug it, by blowing a stream of compressed air through the sample tube into the furnace. When the tube had been driven in as far as desired the compressed air was disconnected and the gas issuing from the tube because of the pressure inside the furnace was sampled; the rate of flow of the gas was regulated by the gate valve at the end of the sample tube. Samples were then taken as the tube was withdrawn until the end of the tube was at the wall or until the tube became plugged with slag or jammed by the descending stock.

ANALYSIS FOR CYANIDE

Samples for ordinary gas analyses were collected over mercury. A slightly more elaborate apparatus was required for a cyanide determination. At the temperatures (900° to 1,500° C.) prevailing in the lower parts of the furnace the alkali cyanides exist as gases. After withdrawal from the furnace, however, the gases quickly cool and the cyanide vapor condenses to a fume. Hence, when an analysis for cyanide was to be made this fume had to be filtered from the gas. The filter finally used was a paper extraction thimble—1.3 by 3.7 inches, such as used in a Soxhlet extractor—mounted in a suitable holder. Figure 3 shows the design of the holder. A number of these filters with holders were provided to permit quick change and the taking of several cyanide samples with one insertion of the sample tube. The volume of the gas from which a given quantity of cyanide was filtered was determined by means of a dry gas meter which registered 0.1 cubic foot per revolution and was placed in series with and following the filter.

After the cyanide sample was collected, the solution obtained by leaching out the filter was analyzed for total alkali and cyanide. If the material caught by the filter could not be analyzed at once the filter was sealed in an air-tight glass container until analyses could be made. Some of the analyses were made in the laboratory of the blast furnace at Holt, Ala., and some in the fixed-nitrogen research laboratory in Washington, D. C. Total alkali was determined by a simple titration with standard sulphuric acid, methyl orange being used as an indicator. Cyanide was determined by the method of Lundell and Bridgeman.[26]

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[25] Perrott, G. St. J., and Kinney, S. P., "Combustion of coke in the blast-furnace hearth": Trans. Am. Inst. Min. and Met. Eng., vol. 69, 1923, pp. 543–548.

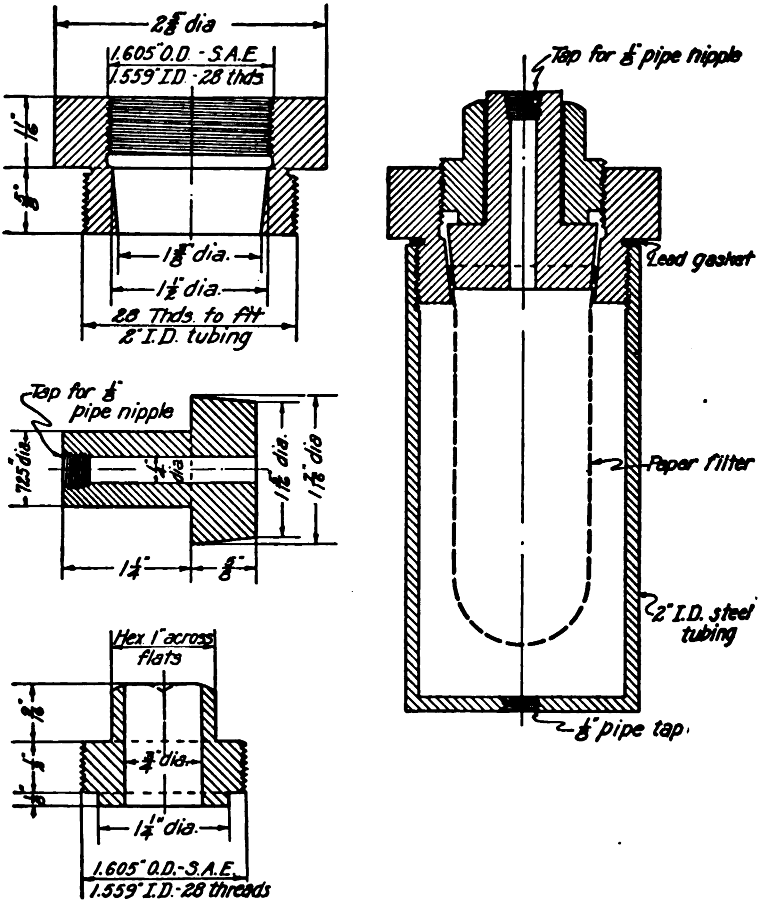

FIGURE 3.—Holder for fume filter

POSSIBLE ERRORS IN ANALYSIS

At the beginning of the investigation the errors that might arise in the method of determining cyanide and alkali in the blast-furnace gases were considered. Some of the chief sources of possible error were thought to be the following: (1) Incomplete filtration, the finer fume might pass through the filter; (2) settling of fume in the gas-sampling tube before the gases reached the filters; (3) the projection of solid or liquid particles containing cyanide or alkali through the tube and into the filter; (4) conversion of cyanide to carbonate by the action of CO while the cyanide and CO are cooling in the sample tube, with the result that the determined percentage of alkali combined with cyanide is lower than the percentage actually combined in the furnace.

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[26] Lundell, G. E. F., and Bridgeman, J. A., "A new method for determination of hydrocyanic acid and the alkali cyanides": Jour. Ind. and Eng. Chem., vol. 6, 1914, p. 554.

As to (1), numerous tests made with fume-laden gas taken from the slag notch indicated that with the type of filter finally adopted no fume remained in the gas. In these tests the gas after passing the filter was bubbled through water without developing any alkalinity in the water.

As to (2), occasional tests have shown that there is some settling, but the error in most samples is probably less than 10 per cent. This opinion is based on the amount of alkali found when the iron sample tube and the short length of rubber tube leading from it to the filter was washed out after several determinations. With a gas flow of approximately 0.5 cubic foot per minute, an average rate used, it is calculated that a given portion of gas requires less than two seconds to pass the length of the tube, so that one may expect most of the fume to reach the filter.

To ascertain the seriousness of (3) the alkali content of the solid material that might be thrown out may be estimated. If we assume that a condition of equilibrium has been reached, then in any given period of time the amount of alkali moving downward past a certain point must equal that moving upward in the gases, plus that passing out in the slag, minus that passing out in the top gases. On such a basis it is calculated that in this furnace an alkali concentration in the gas equivalent to 3.5 ounces per 1,000 cubic feet corresponds to a total alkali oxide content of the descending stock of not more than 1 per cent. Hence, in an experiment in which 1 cubic foot of gas containing 0.0035 ounce of KCN is collected an error of only 10 per cent would be caused by the projection into the filter of 0.035 ounce of charge containing the average alkali content. As, according to the authors' observation, very little of such material reached the filter, it is believed that the error was small.

With respect to (4), no quantitative information is at hand as to the rate at which the equilibrium between CO, N_2, Na_2CO_3, and NaCN is established, and hence the authors are uncertain as to what part of the cyanide in the furnace is converted to the carbonate during cooling. As, however, some samples were obtained in which almost 100 per cent of the alkali remained as cyanide, it seems probable that the error from this source is not great.

The reader will note that all of these possible sources of error except (3)—the projection of solid charge into the filter—tend to give low results. The findings as to the concentration of cyanides in the furnace can therefore be regarded as conservative.

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NUMBER AND RESULTS OF ANALYSES FOR CYANIDE

The following determinations of the cyanide content of the blast-furnace gases were made: Twenty-three determinations at hole 4, at the base of the mantle and 19¼ feet above the plane of the tuyères; 19 determinations at hole 5, or 2¼ feet above the plane of the tuyères; 38 determinations in the plane of the tuyères; 8 determinations on gas from the slag notch; and 5 determinations on top gas.

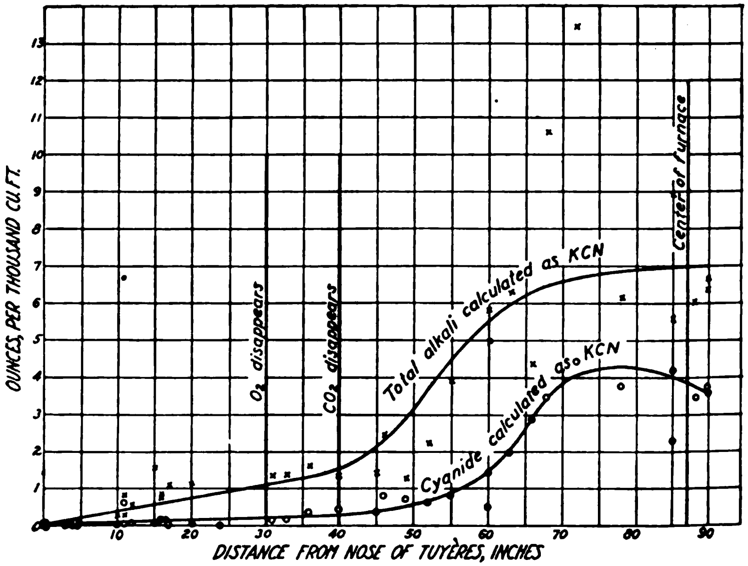

Figure 4.—Cyanide and alkali in gases at the tuyère plane. (See Table 8)

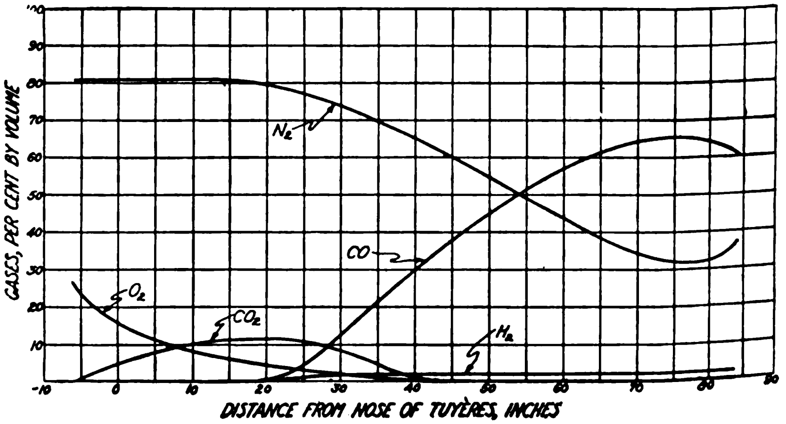

Figure 5.—Analysis of gas at the tuyère plane (plane 6)

The determinations at planes 4, 5, and 6 differ from all previous measurements known to the authors. The samples were taken at varying distances from the wall and fume blowing through a hole in the wall as heretofore. This distinction is important, because at certain levels of the furnace the concentration in the interior is quite different from that at the wall. A large number of gas samples from various planes in the furnace were analyzed for N_2, CO, CO_2, O_2, and H_2. Some of these samples were taken at the same time as the cyanide samples and some were taken independently.

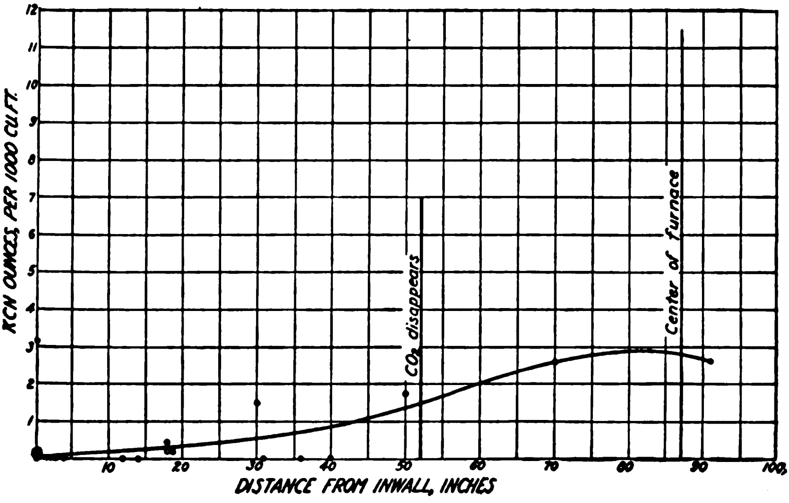

FIGURE 6.—Cyanide in gases at plane 5. (See Table 9)

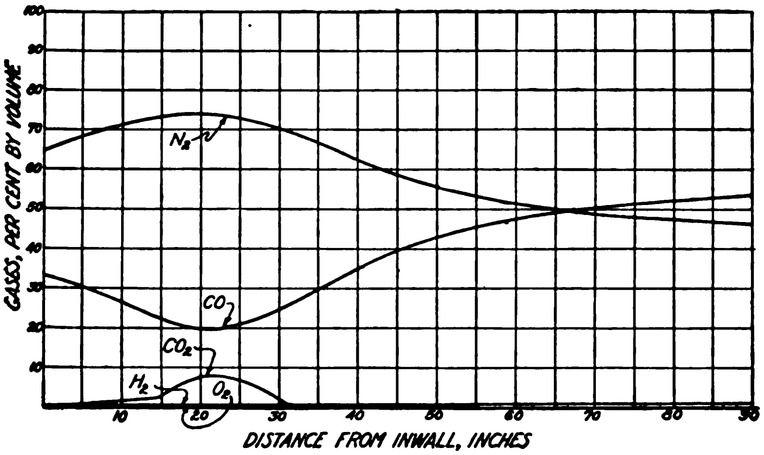

FIGURE 7.—Analysis of gas at plane 5

The results for cyanide and alkali are shown in Tables 8, 9, and 10 and Figures 4, 6, and 8, and the results of the gas analyses in the curves of Figures 5, 7, and 9.

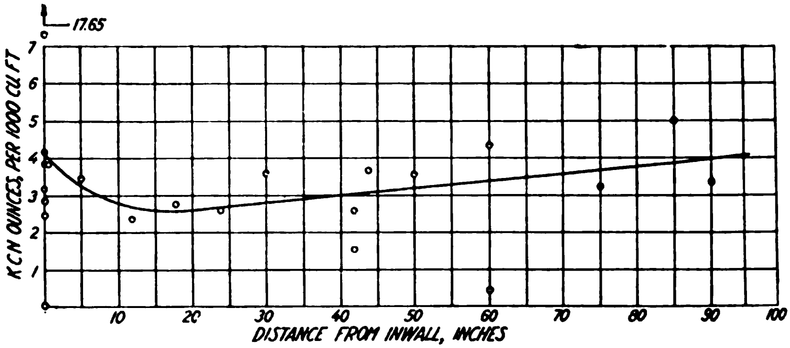

FIGURE 8.—Cyanide in gases at plane 4

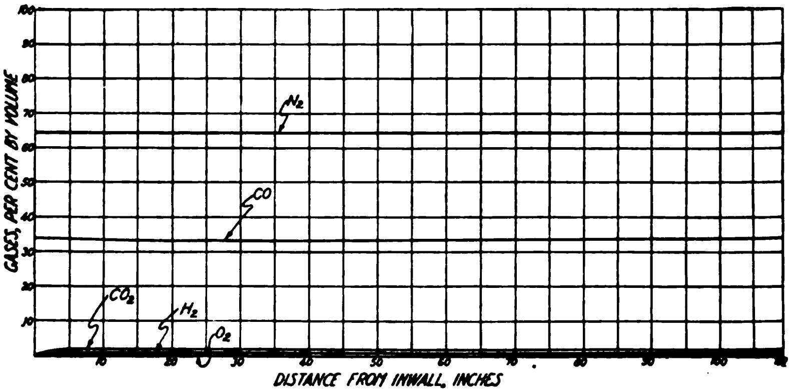

FIGURE 9.—Analysis of gas at plane 4

TABLE 8.—*Cyanide and alkali in the gases at the tuyère plane of a southern furnace*

Distance from nose of tuyère, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounce per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent	Distance from nose of tuyère, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
0	1.0	0.110	(1)		40	0.3	1.38	0.494	36
0	.3	.076	0.035	46	45	1.0	1.45	.389	27
0	1.0	.076	(1)		46	1.2	2.47	.812	33
3	3.0	.106	.035	33	49	2.0	1.30	.706	54
4	.6	.076	.035	46	52	1.0	2.26	.636	28
4	.1	.076	.035	46	55	3.0	3.92	.848	22
10	.1	.247	.035	14	60	1.0	4.98	1.45	29
11	1.0	.272	.081	30	60	.75	5.84	.501	9
11	.2	.812	.635	78	63	3.1	6.32	1.94	31
12	.3	.565	.076	13	66	1.1	4.380	2.86	65
15	2.0	1.590	.076	5	68	1.2	10.60	3.50	33
16	.1	.812	.106	13	72	1.0	.265	.062	23
16	.1	.777	.106	14	72	3.0	13.47	4.42	33
17	1.0	1.100	(1)		78	.9	6.18	3.75	61
20	2.5	1.130	.053	5	85	3.0	8.960	4.17	47
24	2.0	.134	(1)		85	3.0	5.58	2.30	41
31	3.2	1.38	.106	8	88	.4	6.01	3.46	58
33	1.5	1.38	.166	12	90	.5	6.68	3.74	56
36	.1	1.62	.388	24	90	1.0	6.39	3.60	56

[1] Titration, one drop only; cyanide less than 0.0005 ounce per 1,000 cubic feet.

TABLE 9.—*Cyanides and alkali in the gases at plane 5 of a southern furnace*

Distance from in-wall, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounce per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent	Distance from in-wall, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
0	5	0.424	0.087	21	18	0.4	3.39	0.420	12
0	1	1.00	.056	6	18	.4	.251	.124	49
0	3	.830	.131	16	30	1.0	1.91	1.48	77
0	4	.660	.120	18	31	.5	.476	(1)	---------
0	1	.325	.058	18	40	1.0	.597	(1)	---------
0	1.6	---------	.311	18	36	1.0	.897	(1)	---------
4	1	.657	(1)	---------	50	1.1	2.44	1.73	71
12	.5	1.81	(2)	---------	70	1.4	---------	2.54	---------
14	1.0	.239	(1)	---------	91	.8	---------	2.54	---------
18	.4	.417	.166	40					

[1] Titration, one drop only; cyanide less than 0.019 ounce per 1,000 cubic feet.
[2] Titration, one drop only; cyanide less than 0.038 ounce per 1,000 cubic feet.

TABLE 10.—*Cyanides and alkali in the gases at plane 4 of a southern furnace*

Distance from in-wall, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent	Distance from in-wall, inches	Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent
0	3.0	0.067	0.067	100	18	0.5	4.52	2.77	61
0	4.0	5.26	4.16	79	24	.2	5.57	2.65	46
0	5.0	---------	7.80	---------	30	1.0	---------	3.60	---------
0	5.0	15.35	14.70	96	35	2.0	---------	2.90	---------
0	5.0	21.50	17.65	82	42	.6	2.36	1.58	67
0	12.0	14.80	10.93	74	42	.1	4.16	2.61	63
0	1.1	3.53	2.82	80	44	.6	---------	3.67	---------
0	1.6	5.30	3.88	73	50	2.0	---------	3.57	---------
0	2.0	4.24	2.47	58	60	3.1	---------	4.31	---------
0	.3	5.65	3.18	56	60	.3	.99	.402	41
0	.6	5.30	3.88	73	75	.4	---------	3.25	---------
5	1.2	---------	3.49	---------	85	1.1	---------	4.95	---------
12	.2	4.13	2.04	49	90	1.2	---------	3.35	---------

CHECKING OF RESULTS BY LARGE-SCALE COLLECTION OF FUME

The results for plane 4 were checked by a number of experiments in which the fume was collected from a large volume (30,000 to 80,000 cubic feet) of gas taken at an average rate of flow of about 200 cubic feet per minute. Figure 10 gives a sketch of the fume collector, which consisted essentially of a series of baffles and copper-wire screens of progressively increasing fineness contained in a welded sheet-iron box, whose dimensions are shown in Figures 11 and 12. When the side of the box was removed the screens and baffles were slid into place in tightly fitting guides. As the openings in the baffles were alternately at the top and bottom, the gas had to take a tortuous course through the screens. In some of the earlier experiments fume could be seen in the exit gas, and in later experiments a number of the final screens were replaced with asbestos cloth. As, however, the results were about the same after the change, the loss of fume in the apparatus as shown could not have been great. The collected fume was removed at the end of each experiment by detaching the side of the box.

After leaving the collector the gases passed through an orifice meter that measured the flow. As the rate of flow fluctuated considerably, and as readings of the meter could not be taken continuously, the volume of gas passed is uncertain within perhaps 10 per cent.

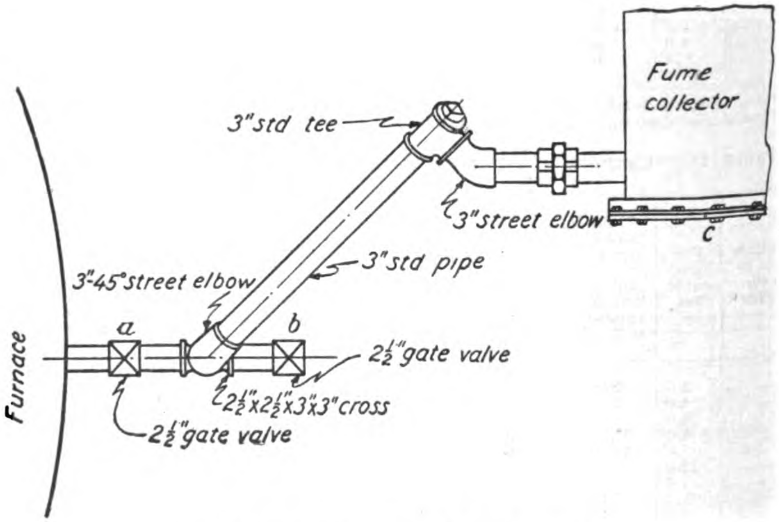

FIGURE 10.—Pipe connections for fume collector

Figure 10 shows the connections from the furnace to the collector. The rate of gas flow was regulated by the valve *A*. Occasionally the pipe became clogged with stock from the furnace, and then a rod had to be inserted through valve *B* to clear out the obstruction. For convenient use of the rod the elbow between *A* and *B* was turned so that the collector did not stand in front of these valves. The inclination of the pipe leading to the collector was such that the bottom of the box rested on the operating platform, which was about 18 inches below the pipe from the furnace.

Table 11 shows the results of the experiments with this apparatus. The agreement between different tests is as good as would be expected. The experiments were made over a period of several months, so that this agreement indicates that the cyanide concentration at plane 4 does not fluctuate widely from month to month. The average concentration of cyanide indicated by these large-scale tests agrees well with the results of the small-scale sampling. (See fig. 8.)

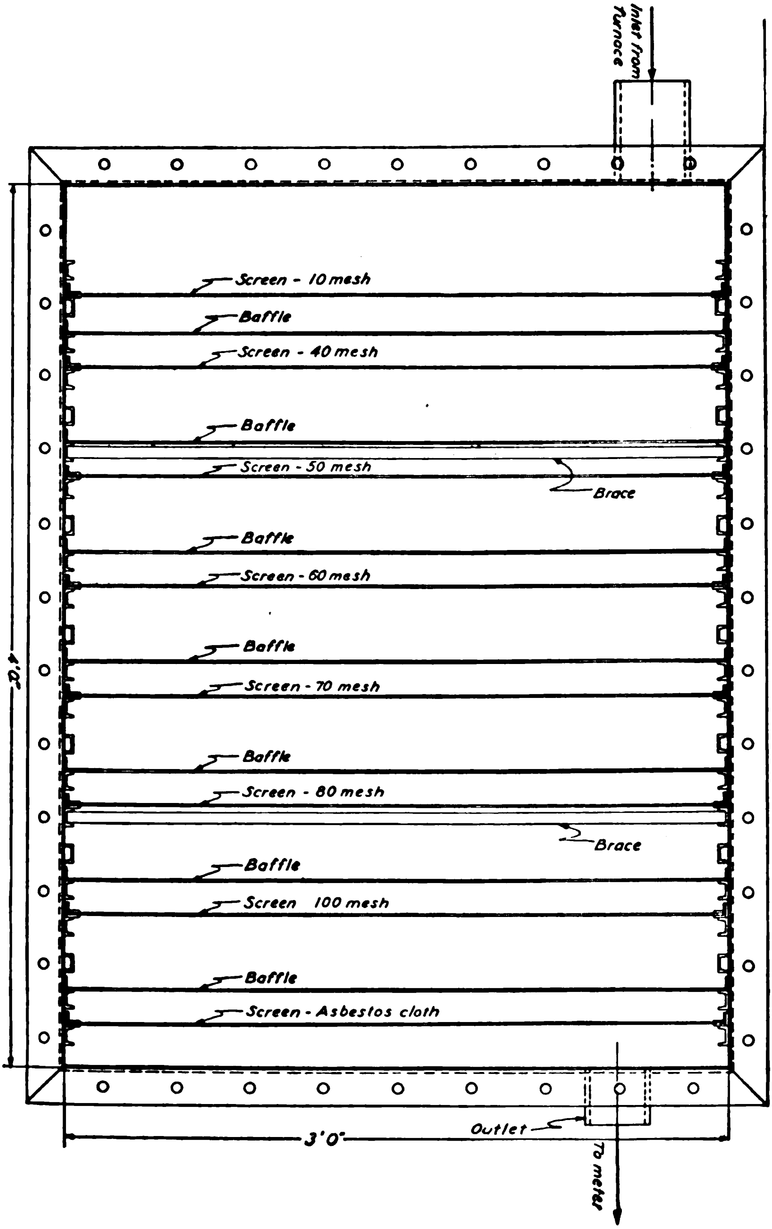

FIGURE 11.—Enlarged section of collector

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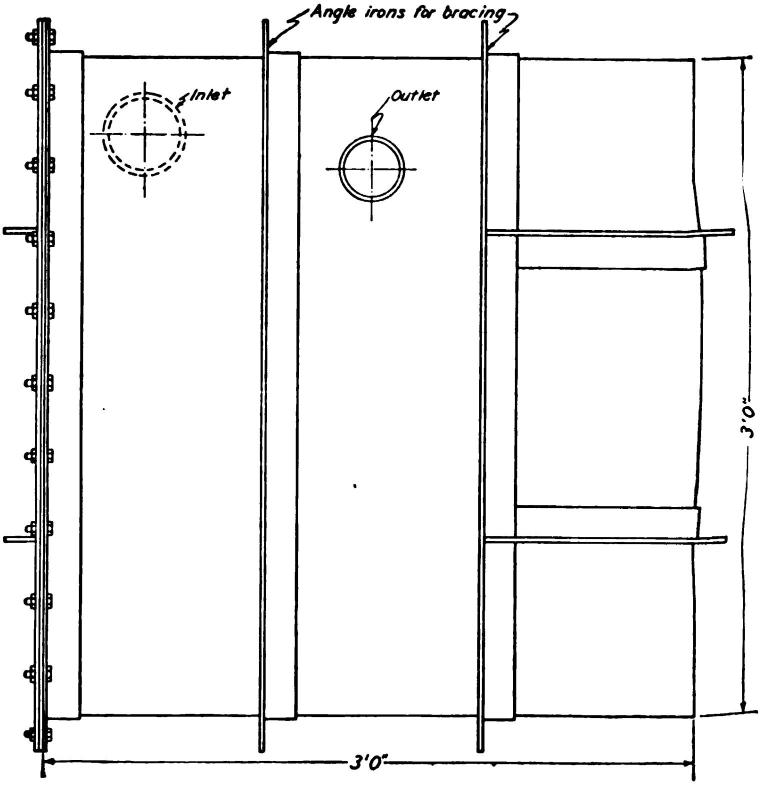

FIGURE 12.—End section of collector

TABLE 11.—*Results of large-scale collection of fume*

Experiment No.	Duration of test, minutes	Volume of gas passed, cubic feet	Average flow, cubic feet per minute	Material collected, pounds	Total alkalinity as KCN, per cent	Cyanide, calculated as KCN, per cent	Per cent of alkalinity due to cyanide	Per cent water-soluble	Concentration of cyanide, ounces KCN per 1,000 cubic feet
1	360	79, 200	200	55. 61	58. 4	31. 3	53. 6	74. 6	3. 52
2	245	34, 790	142	17. 25	65. 8	39. 7	60. 3	75. 1	3. 15
3	320	73, 600	230	80. 50	26. 6	16. 0	60. 1	[1] 29. 2	2. 80
4	342	50, 958	149	26. 88	79. 8	50. 0	62. 7	86. 7	4. 22
5	160	38, 720	242	17. 57	73. 2	41. 2	56. 3	88. 0	2. 99
Average [2]					69. 3	40. 5	58. 2	81. 1	3. 47

[1] Large amounts of stock mixed with collected fume.

[2] Excluding experiment 3.

The average alkali content of the top gas may be calculated from data previously given and from operating data. On the assumption (1) that 8,426 pounds of charge containing the equivalent of 0.53 per cent of K_2O is fed per ton of metal produced, (2) that the daily production of metal is 290 tons, and (3) that the volume of top gas is

38,000 cubic feet per minute (based on the carbon consumption and the analysis of the gas), it is calculated that the top gas should carry alkali compounds equivalent to 2.5 ounces of KCN per 1,000 cubic feet. The amounts actually found in the top gas were very much less, probably because these tests were all made during quiet operation, whereas most of the alkali seems to be lost from the top in furnace slips, as previously shown by data on the concentration of alkali cyanide in the wash water of the wet dust collector. (Table 7.)

Table 12 shows the results of a number of tests of the gases issuing from the slag notch of the furnace. In these experiments the sample tube did not extend into the interior of the furnace, but an iron pipe about 1 inch in diameter was forced into the cinder notch. The fume condensed during the cooling of the gas in passing through and the gas volume was measured as the gas blew through the pipe. The samples were obtained about one hour after cast. It is possible that the high results in the first two tests were due to condensation of fume inside and around the slag notch prior to the taking of the samples.

TABLE 12.—*Cyanide and alkali in gas from slag notch of a southern furnace*

Volume, cubic feet	Total alkali, ounces per 1,000 cubic feet, calculated as KCN	Cyanide, ounces per 1,000 cubic feet, calculated as KCN	Alkali as cyanide, per cent	Remarks
0.67	883	558	63	Tuyère above slag notch closed; sample 66 per cent KCN.
1.34	152	56.5	37	Tuyère above slag notch closed; gas pressure, 5 pounds.
28.1	11.6	9.54	82	Tuyère above slag notch in operation; 72 per cent KCN.
20 (estimated)	20.4	19.0	93	47 per cent KCN.
0.8	23.6	(1)	----------	
13.4	3.26	.99	30	
2.1	23.0	14.82	64	
1.6	14.8	10.93	74	

[1] Titration, 1 drop only; cyanide, less than 0.053 ounce per 1,000 cubic feet.

CONCENTRATION OF ALKALI IN STOCK SAMPLES

It should be possible to calculate the alkali content of the stock in the furnace, because, as previously explained, in a given time the alkali passing down past a given point must be, on the average, equal to that passing upward in the gas past the same point, plus that passing out in the slag, minus that passing out with the top gases. At plane 4 the concentration of alkali is about 5.83 ounces (calculated as KCN) per 1,000 cubic feet, if it is assumed that the cyanide is 60 per cent of the total alkali and the volume of blast is about 35,000 cubic feet per minute (based on carbon consumption and the analysis of the gases); hence there are 2.75 pounds per minute passing upward in the gas. As was shown above, the alkali fed to the furnace is equivalent to 60.1 pounds of KCN (43.5 pounds of K_2O) per ton of metal produced, or $60.1\times\frac{290}{60\times 24}=12.12$ pounds per minute. About 46 per cent of this alkali, or 5.57 pounds per minute, passes out the top and 6.55 pounds per minute into the slag. Hence the alkali (calculated as KCN) moving down past plane 4 in a minute should be, according to the above formula, $12.75+6.55-5.57=13.73$ pounds. On the assumption that all moisture, all of the CO_2 of the limestone, and 80 per cent of the O_2 of the iron oxide have been lost above plane 4, the total weight of stock passing that plane is 1,297 pounds per minute. The total alkali content (cyanide, silicate, carbonate) of the charge should therefore be equivalent to about 1 per cent of KCN.

A considerable number of samples of stock were obtained through hole 4 by opening the sample hole and allowing the solid material to blow out of the hole. Solid material was also hooked out of the furnace by means of a bent bar. The samples were caught in a closed container and cooled in an atmosphere of furnace gas containing about 33 per cent of CO.

These samples were of interest primarily for showing the progress of reduction of the iron oxides and the composition of the metal and of the slag at the point of sampling. It had been hoped that a determination of the alkali content would also provide a valuable check on the reliability of the determination of the alkali and concentrations of cyanide in the gas, but to get a stock sample that was not mixed with fume that had been deposited in and around the sample hole proved extremely difficult. The alkali content therefore was surprisingly high in some of these stock samples. In most tests only that portion of the alkali which dissolved in water and could be titrated with sulphuric acid was determined. Analyses of some of these samples appear in Table 13.

TABLE 13.—*Cyanide content and alkalinity of stock samples*

	Sample No.—									
	1	2	3	4	5	6	7	8	9	10
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Water-soluble alkalinity, calculated as KCN	17.61	3.68	8.04	12.83	--------	--------	--------	--------	--------	--------
Cyanide, calculated as KCN	9.65	.27	1.14	4.43	7.41	9.57	0.7	0.15	0.46	0.48

The water-insoluble portion of sample 3 contained 5.68 per cent of K_2O and 1.19 per cent of Na_2O. Sample 2 contained 8.17 per cent of water-insoluble alkali, calculated as K_2O.

These results are valuable, as they confirm the presence in the furnace of considerable concentrations of cyanides and other alkali compounds. It does not appear, however, when the difficulties of sampling the stock are considered, that the accuracy of the gas sampling ought to be seriously questioned because the alakali content of some of the stock samples is unexpectedly high. This view is strengthened by the fact that the results of the large-scale collection of fume in the apparatus illustrated by Figure 10 checks satisfactorily the small-scale sampling with the water-cooled sample tube.

COMPOSITION OF BLAST-FURNACES FUMES

Four samples of fume from hole 4, which were condensed by the apparatus of Figure 10 and were relatively free from stock carried over mechanically were analyzed in some detail. These analyses appear in Table 14, with a similar analysis of a sample of fume from the slag notch.

TABLE 14.—*Analyses of fume from a southern furnace*

	From fume collector of hole 4				From slag notch
	1	2	3	4	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Moisture	----------	3.34	3.38	----------	----------
Water-soluble portion:					
Potassium cyanide (KCN)	31.42	44.60	46.20	39.58	46.4
Potassium carbonate (K_2CO_3)	24.60	16.33	24.68	31.95	[1] 13.8
Sodium carbonate (Na_2CO_3)	1.24	8.08	6.67	6.92	4.0
Silica (SiO_2)	0	.12	.37	.04	.16
Alumina and iron oxide (R_2O_3)	.64	.57	.72	.51	1.46
Zinc oxide (ZnO)	13.18	3.98	4.47	3.73	5.43
Lime (CaO)	.57	.29	.30	.33	.46
Magnesia (MgO)	3.08	(2)	(2)	(2)	.97
Water-insoluble portion:					
Silica (SiO_2)	.98	2.86	1.18	.23	1.00
Lead oxide (PbO)	12.30	1.78	1.75	1.15	----------
Alumina and iron oxide (R_2O_3)	3.83	5.89	3.45	1.07	1.11
Zinc oxide (ZnO)	4.71	.13	.14	.04	2.49
Lime (CaO)	.65	.37	.31	.08	.24
Magnesia (MgO)	.01	1.20	1.15	.60	.03
Soda (Na_2O)	.58	.42	.17	.07	.10
Potash (K_2O)	1.02	.58	.57	.11	.29
Carbon, free (C)	----------	4.57	1.13	1.07	----------
Total	98.81	95.11	96.64	87.48	77.94

[1] NaCN.

[2] Trace.

Samples 2, 3, and 4 above were obtained within a few days of one another, while sample 1 was taken several months before. These analyses indicate that the composition of the fume is relatively constant over a short period but may vary considerably over longer periods. It is noted in particular that the proportion of zinc is much higher in sample 1 than in any of the others, and that the magnesia in this sample is virtually all water soluble.

The fume from the slag notch appears to differ qualitatively from that from hole 4, chiefly in the absence of lead. The higher percentage of alkali combined as cyanide, as shown in this sample from the slag notch, is not typical of fume at this point. As shown in Table 10, the percentage of the total water-soluble alkali which is combined as cyanide ranges from 37 to 93 per cent.

Besides the large samples of fume collected at hole 4, several small samples were collected which may likewise be indicative of the quality of material that might be collected there. Samples 1 and 2 in Table 15 were deposited on the inside of the sample hole and samples 3 and 4 were obtained from inside the valve that closed the sample hole when samples were not being taken. Partial analyses show the following results (Table 15):

TABLE 15.—*Partial analyses of additional fume*

	1	2	3	4
	Per cent	*Per cent*	*Per cent*	*Per cent*
Potassium cyanide (KCN)	55.2	23.1	50.8	42.10
Potassium carbonate (K_2CO_3)	16.70	19.1	25.2	35.78
Sodium carbonate (Na_2CO_3)	1.05	--------	0	3.33
Water-soluble silica (SiO_2)	0	.23	--------	.35
Undetermined water soluble	11.10	.50	14.0	--------
Water-insoluble potash (K_2O)	--------	--------	.79	--------
Water-insoluble soda (Na_2O)	--------	--------	1.46	--------

In analyses 3 and 4 there was evidence of considerable amounts of lead and zinc, but no determinations of these elements were made. It is an interesting fact that all samples of fume examined contained much more K than Na, though in the original charge the two elements were present in about equivalent amounts. In other words, the tendency of the potassium compounds to volatilize and circulate in the furnace is much greater than that of the sodium compounds. This is in accord with the known greater volatility of potassium compounds.

Table 16 compares the above analyses with analyses reported by Bell[27] of samples of fume from different heights in the blast furnace.

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[27] Bell, I. Lowthian, Principles of the Manufacture of Iron and Steel. London, 1884, p. 225.

TABLE 16.—*Composition of fume at the Clarence, England, furnace, according to Bell*

	Emitted from slag	Height above tuyères, feet					Escaping gases, 76 feet
		2	26.5	39.75	45.5	58.25	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Sulphuric acid, free (H_2SO_4)	5.00						
Phosphoric acid (H_3PO_4)							1.57
Potassium sulphate (K_2SO_4)	85.00						1.00
Sodium sulphate (Na_2SO_4)	7.50						.23
Magnesium sulphate ($MgSO_4$)	2.50						
Lead sulphate ($PbSO_4$)							1.87
Potassium cyanide (KCN)		75.98	89.20	71.21			
Sodium cyanide ($NaCN$)			3.51	.07			
Potassium carbonate (K_2CO_3)		3.95					2.61
Sodium carbonate (Na_2CO_3)		20.70	3.52	3.91			
Calcium carbonate ($CaCO_3$)							(?)
Ammonium chloride (NH_4Cl)							2.39
Potassium chloride (KCl)		.55			5.42	1.80	5.92
Sodium chloride ($NaCl$)			2.48	6.20	2.93	1.00	1.48
Magnesium chloride ($MgCl_2$)							1.56
Zinc oxide (ZnO)		(1)	(1)	6.71	15.27		13.39
Zinc carbonate ($ZnCO_3$)				11.88		17.17	
Zinc sulphide (ZnS)							7.70
Zinc, metallic (Zn)					50.75	13.66	
Zinc chloride ($ZnCl_2$)					7.65	13.16	4.95
Calcium chloride ($CaCl_2$)							2.06
Lead chloride ($PbCl_2$)					1.47	8.77	
Calcium sulphate ($CaSO_4$)					(1)	.57	3.60
Silica (SiO_2)					6.38	15.00	10.25
Lime (CaO)					6.70	14.37	.56
Alumina (Al_2O_3)					1.84	6.11	3.66
Magnesia (MgO)					.31	4.33	(1)
Ferrous oxide (FeO)					1.03	2.63	
Ferric oxide (Fe_2O_3)							15.00
Potassium iodide (KI)							.12
Carbon (C)					.27	.41	13.66
Water (H_2O)							6.42
Total	100.00	101.18	98.71	99.98	100.02	98.98	100.00
Approximate temperature, degrees Fahrenheit			2,000	1,800	1,600	900	600
Fume per 1,000 cubic feet, ounces		13.61	7.74	2.27	1.39	1.65	1.903

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[1] Trace.

DISCUSSION OF EXPERIMENTAL RESULTS

In the light of the data that have been presented, the effect of accumulation of alkali cyanides on the operation of the furnace and the technical and economic feasibility of recovering alkali cyanides as a blast-furnace by-product will now be considered.

As the feasibility of recovering cyanide will largely be determined by the effect of this recovery on the production of iron by the furnace, the matter of furnace operation will be considered first.

INFLUENCE OF ALKALI CYANIDES ON OPERATION OF THE BLAST FURNACE

EFFECT ON FURNACE LININGS

Volatile alkaline compounds, the cyanides particularly, have been thought to contribute largely to the deterioration of the furnace lining. The first "hot spots" often develop near the base of the mantle, where, as shown, there is considerable deposition of alkaline compounds from the gases. Moreover, these hot spots as a rule develop in considerably shorter time in southern than in northern furnaces, and one is led to inquire whether this difference may not be due, in part, to the raw materials used in the southern furnaces being generally higher in alkali. Published analyses of bricks taken from points in blast-furnace linings where failure has occurred have contained considerably more alkali than the original bricks, as is shown by Table 17.

TABLE 17.—*Effect of alkali on blast-furnace lining*

	Firmstone [1]			Osann [2]	
	Before use	After use—30 feet above hearth		45 feet above hearth	
		Glazed skin $\frac{1}{32}$-inch thick	Body of brick	Before use	After use
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Silica (SiO_2)	56.12	40.23	57.63	55.7	55.7
Alumina (Al_2O_3)	37.48	12.22	31.64	33.5	30.0
Ferric oxide (Fe_2O_3)	4.43	11.93	3.73	4.00	3.0
Lime (CaO)	.36	10.92	.24	.37	.23
Magnesia (MgO)	.29	4.31	.11	1.21	.95
Potash (K_2O)	.99	9.39	2.59	2.60	5.30
Soda (Na_2O)	.23	8.43	.51	.45	1.67
Metallic iron (Fe)			1.51		
Zinc oxide (ZnO)			.59		
Chlorine (Cl)					.04
Carbon (C)					3.24

[1] Firmstone, Frank, "An example of the alteration of fire brick by furnace gases": Trans. Am. Inst. Min. Eng., vol. 34, 1904, pp. 427–431.

[2] Osann, B., "Einwirkung Zustärender Einflüsse auf Feuerfestes Mauerwerk im Hüttenbetriebe" Stahl und Eisen, Bd. 23, 1903, pp. 823–829.

An increase in the alkali content of the bricks of the lining would be detrimental because (1) the softening temperature of the surface of the bricks would be lowered and abrasion correspondingly increased; and (2) the binding between bricks would be softened and weakened, so that whole bricks might be loosened from their position. The analyses quoted from Firmstone show, in fact, that in the interior of the blast-furnace wall the alkali content is considerably greater along joints between bricks than in the body of a brick.

It would seem, then, that a substantial reduction in the amount of volatile alkali compounds in circulation and a corresponding reduction in the concentration of alkali in the stock would increase somewhat the life of the lining.

EFFECT ON FUEL ECONOMY

Franchot[28] has suggested that the formation and circulation of cyanides in the furnace causes a significant increase in fuel consumption. The alkaline cyanides are formed by reactions that are endothermic. Hence, if the cyanides are formed and volatilized in the bosh, where the heat absorption determines the coke consumption of the furnace, and are decomposed and condensed in the shaft, the effect on the fuel economy is obviously that suggested by Franchot. If accumulation continues until a large amount of alkaline material is being circulated in this manner, the effect might be of great practical importance.

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[28] Franchot, Richard, Economic Significance of Cyanide Accumulation in the Blast Furnace: Preprint 1470-C, Am. Inst. Min. Met. Eng., July, 1925.

The amount of alkali actually found in the present furnace was, however, much less than that assumed by Franchot in his calculation, and was too small to affect the fuel economy appreciably. Figures 4 and 6 show that in the tuyère plane, and also the plane 2 feet 3 inches above the tuyères, the maximum concentration of alkali cyanide is of the order of about 3 ounces per 1,000 cubic feet. This maximum occurs at the center of the furnace, where the flow of gas is known to be relatively small, and hence the total cyanide passing upward, away from the hearth, is much less than the product of this concentration by the total flow of gas. However, in order to err on the high side, the assumption is made that the distillation of alkali cyanide is represented by this product, and from this the heat effect is calculated. It is estimated that the heat of the reaction

$$\underset{\text{liquid}}{K_2SiO_3} + \underset{\text{solid}}{CaO} + 3C + N_2 = \underset{\text{liquid}}{CaSiO_3} + \underset{\text{gaseous}}{2KCN} + CO \qquad (3)$$

is approximately −70 kilogram calories. The total volume of gas leaving the hearth is approximately 35,000 cubic feet per minute. The total absorption of heat for cyanide formation and volatilization is hence

$$\frac{3\times454\times35000}{2\times65\times16\times1000}\times70=1{,}605 \text{ kilograms calories per minute.}$$

In the same length of time about 530 pounds of coke is burned. Under the conditions assumed by Franchot the available heat produced in the hearth at 1,500° C. is about 1,000 kilogram calories per pound of coke burned, or $530\times1{,}000=530{,}000$ kilogram calories per minute. In this furnace the formation and volatilization of KCN from the hearth dissipates not more than $\frac{1{,}605\times100}{530{,}000}=0.3$ per cent of the available heat of the hearth, a negligible figure.

EFFECT ON REDUCTION OF IRON

The alkali cyanides are powerful reducing agents, and this fact early led to the suggestion that cyanides may play an essential rôle in the furnace in reducing the final portions of iron oxide.[29] Bell,[30] who studied this point, rather inclined to the view that cyanides were not essential for this final reduction. He based his conclusion mainly on the observation that when a new furnace is blown in a good grade of iron is being produced before enough time has elapsed to permit a significant accumulation of alkali compounds in the furnace. In the present investigation, an examination of the results of gas and stock sampling showed that at plane 4 about 20 per cent of the iron oxide remained unreduced. In order to reduce the final 20 per cent of iron by cyanide the gases in the bosh would have to contain at least 50 ounces of KCN per 1,000 cubic feet. The concentrations actually found were much lower, hence it seems unlikely that the cyanides were effecting any considerable reduction. The upper sections of the bosh, however, were not explored, and it is possible that in this part of the furnace concentrations somewhat higher than those found were present.

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[29] Forsythe, Robert, The Blast Furnace and the Manufacture of Pig Iron, revised by C. A. Meissner and J. A. Mohr. New York, 1922, pp. 224–226.

[30] Bell, I. Lowthian, Chemical Phenomena of Iron Smelting. London, 1872, p. 141.

RELATION OF CYANIDE FORMATION AND DECOMPOSITION TO VARIATION IN OXYGEN-NITROGEN RATIO

The molecular ratio of nitrogen to oxygen in the air supplied the blast furnace was calculated to be 3.80. In the furnace the O_2 quickly combines as CO and CO_2, but the ratio of N_2 to total O_2 (free and combined) should remain the same unless chemical changes occur which increase or decrease the concentration of O_2 or N_2 in the gases. The change in this ratio is, therefore, of interest as a rough index of the type of reaction that occurs in various parts of the furnace. This ratio has been calculated from the analysis of gas samples taken at various distances from the wall in planes 4, 5, and 6. The results are shown in Table 18.

TABLE 18.—*Nitrogen-oxygen ratio in blast-furnace gas*

Distance from wall or (in plane 6) from nose of tuyère, inches	Ratio			Distance from wall or (in plane 6) from nose of tuyère, inches	Ratio		
	Plane 4	Plane 5	Plane 6 [1]		Plane 4	Plane 5	Plane 6 [1]
6			3.83	52		2.48	
0	3.69	3.65	4.99	54			2.07
4		4.30		56	3.46		
6	3.55		4.18	58		2.27	
10		4.51		60	3.69		1.68
12	3.71		4.11	65			1.20
15	3.56	4.58		66	3.54	1.94	
18	3.55		4.29	72	3.64		
20		4.76		74		1.86	
24	3.59		4.49	78			.96
25		4.23		80	3.52	1.82	
30	3.76	3.95	3.88	84		1.78	1.22
36	3.71	3.79	3.76	88	3.52		
40		3.68		90		1.71	
42	3.52		3.22	96	3.64		
46		2.66		102	3.45		
48	3.58		3.09	110	3.63		

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[1] Tuyère plane.

How far may the variations in this ratio be due to the formation and decomposition of cyanides? The formation of cyanide decreases the N_2 and increases the O_2 (as CO) content of the permanent gases.

$$K_2O + 3C + N_2 = 2KCN + CO \qquad (2)$$

but the oxidation of cyanide according to the equation

$$2KCN + 3/2\ O_2 = K_2CO_3 + N_2 \qquad (4)$$

adds N_2 and subtracts O_2. Hence if reactions (3) and (4) are considered by themselves, the nitrogen-oxygen ratio should tend to be lower than the air ratio in zones of cyanide formation and higher in zones of cyanide decomposition. Bell[31] first suggested these reactions with the alkali cyanides as part explanation of peculiar variations in this ratio with increasing distance above the tuyères. More recently Franchot[32] based his calculation of the concentration of alkali cyanides in the blast furnace on the observed divergence of the ratio from the air ratio as reported by Perrott and Kinney.[33]

From the data obtained in the present investigation it should be possible to determine whether there is any quantitative correlation between cyanide concentration and gas composition. The cyanide (or alkali) concentration is much too small to account for the alteration in the gas ratio. This conclusion seems beyond doubt, even though it leaves no adequate explanation of certain variations in the ratio observed. For example: At the nose of the tuyère the ratio is 4.99 as compared with the air ratio of 3.80. One cubic foot of air entering the tuyère contains about 1/4.80 cubic foot of O_2 and 3.80/4.80 cubic foot of N_2. Suppose that this cubic foot of air burns KCN, so that x cubic feet of N_2 are produced according to equation (4). At the same time $\frac{3}{2}x$ cubic feet of O_2 disappear from the permanent gas, as equation (4) also shows. The ratio of N_2 to O_2 after this action is in general $\frac{3.80/4.80 + x}{1/4.80 - \frac{3}{2}x}$, and $\frac{3.80/4.80 + x}{1/4.80 - \frac{3}{2}x} = 4.99$; $x = 0.0293$.

In other words, if the ratio discrepancy is to be explained as due to the combustion of cyanide, then each cubic foot of gas at the nose of the tuyère contains about 0.0293 cubic foot of N_2 resulting from this combustion. If the fume of alkali carbonate resulting from the combustion remains in suspension in the gas oven for a short time a concentration of alkali carbonate equivalent to 154 ounces of KCN per 1,000 cubic feet should be found. The amount found at this point was, however, extremely small—of the order of 0.1 ounce per 1,000 cubic feet. Similarly, in order to explain, on the basis of cyanide formation, the low ratio, 1.20, found at 65 inches from the tuyère,

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[31] Bell, I. Lowthian, Chemical Phenomena of Iron Smelting. London, 1872, p. 243.

[32] Franchot, Richard, work cited.

[33] Perrott, G. St. J., and Kinney, S. P., work cited.

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the gas should contain 179 ounces of KCN per 1,000 cubic feet, as compared with about 3 ounces per 1,000 cubic feet actually found. The low ratios at the center of the furnace might possibly be explained as due to the accumulation of CO from the reduction of the final portion of iron and other oxides, but the flow of gas through this region is so low that even a small amount of reduction could cause a large effect on the nitrogen-oxygen ratio. There seems to be, however, no satisfactory explanation of the high ratio near the tuyères if the cyanide combustion theory is abandoned.

PROBABLE EFFECT ON FURNACE OPERATION OF WITHDRAWING GAS FOR RECOVERY OF CYANIDE

Consideration of the facts given above indicates that if any effect is observed when the cyanide concentration in the furnace is lowered it should be beneficial to the life of the lining and to fuel economy, although, as was shown, the effect on fuel economy is negligible in furnaces containing cyanide concentrations no higher than those found in the furnace already studied. If then the view, which seems now generally accepted, that cyanides are not indispensable reducing agents in the furnace is adopted, it may be said that a reduction of cyanide concentration in the furnace would not be detrimental and might be beneficial.

MAXIMUM PRACTICABLE CO_2 CONTENT OF TOP GAS

When, however, we consider the practical means available for removing cyanides—that is, by withdrawing a portion of gas from the lower sections of the furnace—we must note the effect that this removal of gas may have on the operation of the furnace. It is well known that the proportion of CO in the shaft of the furnace is considerably in excess of that required for the reducing reactions there, and consequently it is safe to assume that a considerable proportion of the gas may be withdrawn without interfering with the operation of the furnace. The equilibria involved in the reduction of iron oxides by CO are so complicated that it is impossible to predict the maximum CO_2 content of top gas for satisfactory furnace operation. A few furnaces, however, are operating successfully with a CO_2 content as high as 16.5 per cent.

MAXIMUM FRACTION OF GAS THAT MAY BE WITHDRAWN

The average analysis of the top gas of the furnace studied in the present investigation was 9.9 per cent CO_2, 28.1 per cent CO, 2.0 per cent H_2, and 60.0 per cent N_2. As a basis for speculation we may assume that when a part of the blast-furnace gas is withdrawn the process of reduction in the shaft is not disturbed, and the gas passing from the top still carries the same total quantity of CO_2 as when the entire amount passes up the shaft. It may be readily seen, then, that to raise the CO_2 content from 9.9 to 16.5 per cent, 9.9/16.5 or 60 per cent of the total gas from the bosh should be passed up the shaft. Forty per cent of the gas could be withdrawn at the base of the shaft, leaving enough gas to do the work of reduction. It is tacitly assumed in this calculation that there is no appreciable direct reduction of ore by carbon in the shaft. Moreover, no account has been taken of the fact that some of the CO_2 in the top gas is due to the dissociation of CO to CO_2 and C. If allowance is made for this an even larger fraction of gas might be withdrawn without interfering with reduction in the shaft.

Withdrawal of a part of the gas at the base of the shaft will lower the calorific value as well as the volume of the top gas. If in consequence the volume of the top gas is too small or its quality too poor for adequately heating the blast-furnace stoves, it is always possible to add all or any portion of the withdrawn gas after removal of the fume from it. On the other hand, if the poorer top gas is sufficient for heating, the rich gas withdrawn (containing 33 per cent of CO) would be available as a somewhat higher-grade fuel than ordinary blast-furnace gas.

FEASIBILITY OF THE RECOVERY OF CYANIDES

The preceding consideration of the probable effect that removing cyanides would have on the production of iron by the blast furnace having led to the conclusion that such removal would not be harmful and might be beneficial, the question whether the recovery of significant amounts of alkali cyanides from the blast furnace seems economically and technically feasible remains to be considered.

As shown in detail in Tables 8 and 9 and Figures 4 and 6, the amounts of cyanide found were very small in both the tuyère plane and the plane 2¼ feet above the tuyères, except at the center of the furnace. Even the comparatively high results at the center probably do not represent large amounts of cyanide, because this central region is known to be comparatively stagnant, with little gas passing through it. At plane 4 at the base of the mantle, however (see Table 10 and fig. 8), the gas contained consistently about 3.5 ounces of KCN per 1,000 cubic feet. The total alkalinity of all gas samples taken from this hole was not determined, but analyses of several samples of fume from this plane indicate that about 60 per cent of the total alkalinity is due to KCN. The total alkaline compounds in the gas at this point is therefore 5.83 ounces per 1,000 cubic feet.

COMPARISON WITH RESULTS OF EARLIER INVESTIGATORS

The reader will note that these results differ in two ways from those Bunsen and Playfair and Bell obtained. The first difference is that

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the concentration of cyanides is much lower than those they found. At the point 27 inches above the tuyères the concentration of KCN found ranged from zero to 4 grams per cubic meter. For the same region Bunsen and Playfair found 8 to 10 grams per cubic meter, while Bell found on different occasions and at different furnaces 10 to 75 grams per cubic meter. Although a definite explanation of these large discrepancies is not offered here, the method of sampling that the earlier investigators used might easily have given high results. They obtained samples by allowing fume to blow through holes drilled in the furnace wall. Under these conditions part of the alkali cyanide collected might have been deposited in the sample hole prior to sampling (a condition noticed in this investigation), or in crevices in the wall through which the hole passed, and not have been contained in the gas, as the early investigation assumed. A similar method was used in the present investigation for sampling at the slag notch and it indicated some high concentrations of cyanide, possibly due, as was mentioned earlier, to an error of this sort.

POSITION OF ZONE OF MAXIMUM CYANIDE FORMATION

The second difference between the present results and those of Bell is that he found that the concentration of cyanides decreases continuously with increasing distance above the tuyère plane, whereas the present investigation showed that the maximum concentration is not at the tuyère plane. The highest concentration found was at plane 4, at the base of the mantle. It is not possible to say, of course, that the maximum concentration in the furnace is at this point. It is probable, in fact, that the maximum is at a level somewhat lower than plane 4. The temperature (measured with a thermocouple) at plane 4 is 835° C. at the wall and 905° C. at the center. Although these temperatures more nearly represent the temperature of the stock than that of the gas, and the gas temperature may be somewhat higher, it still seems likely that the temperature of the gas is so low that the vapor pressure of alkali cyanide is very slight. In other words, the condensation and settling of alkali cyanide from the gas probably begins at a level lower than plane 4.

QUANTITY OF ALKALINE COMPOUNDS REMOVABLE

As the present data are insufficient for determining exactly the point of maximum concentration, it will be profitable to consider what amount of alkali compounds can be removed at plane 4. As has been stated, the concentration is about 3.5 ounces of KCN per 1,000 cubic feet, calculated to ordinary temperature and pressure. This concentration will drop somewhat if a part of the gas is continuously withdrawn at plane 4, because removal of some of the alkali compounds from the furnace leaves just so much less alkali to condense in the charge and consequently the amount of cyanide added to the gas as the charge passes downward will be smaller. However, the addition of fresh alkali in the charge will result in a new balance being struck when a given fraction of gas is withdrawn, and the cyanide content of the gas may be nearly as great as when there is no withdrawal. Just how much the concentration is lowered can be determined only by experiment, withdrawing large volumes of gas for a considerable time. In the large-scale fume collection during the present investigation about 0.5 per cent of the total flow was withdrawn. This proportion was too low to show an effect, as about the same concentration was shown by these tests as by the small scale sampling.

CALCULATION OF PROBABLE EFFECT OF CONTINUOUS WITHDRAWAL OF GAS ON CYANIDE CONCENTRATION

In the absence of adequate experimental data on this point it seems desirable to attempt to calculate what effect the withdrawal of a given fraction of gas will have on the concentration of cyanide in the gas. For the purpose of such calculation some relation between the amount of alkali in the charge and the concentration of cyanide found in the gas must be assumed. There is good reason to believe that the amount of cyanide found in the gas is determined largely by the rate at which alkali can be displaced from silicates, and that the cyanide content of the gases at any point where cyanide is being formed is much below the concentration that would be in equilibrium with the liquid phase in the charge at that point. As was shown above, the formation of cyanide may be represented by the equation

$$K_2SiO_3 + CaO + 3C + N_2 = CaSiO_3 + 2KCN + CO. \qquad (3)$$

Throughout that region of the furnace that is here of particular interest the N_2 and CO concentrations are practically constant; as C and CaO are present in excess their concentrations are constant also, and the concentration of $CaSiO_3$ in the liquid phase is also roughly constant. The only variables are the concentrations of K_2SiO_3 in the liquid phase and of KCN in the gas. Therefore the rate of cyanide formation can be roughly represented by the equation

$$R = k_0 K_2SiO_3 - k(KCN)^2.$$

As we are assuming that this reaction is far from equilibrium, the second term in the equation has little effect on the value of R, and we may write as approximately true,

$$R = k_0 K_2SiO_3.$$

As there is such an equation for every point where reaction (3) is occurring, the total concentration C, of alkali, found in the gas at any point will be proportional to the concentration, C′, of K_2SiO_3 at that point:

$$C = k_1 C'. \tag{5}$$

We may also write an equation expressing the fact that the alkali content of the stock is that due to the original alkali in the charge plus that due to the condensation of a part of the fume:

$$C' = C'_0 + K_2(C - c).$$

Here c is the concentration of alkali in the top gas and C'_0 is the percentage by weight of alkali (calculated as KCN) due to the alkali content of the fresh charge. C′ is also expressed in per cent of KCN equivalent. It is reasonable to suppose that the alkali concentration, c, of the top gas will change roughly in proportion to variations in C, the concentration at plane 4. It was estimated above that the concentration in top gas is about 2.5 ounces per 1,000 cubic feet; the concentration at plane 4 is 5.8 ounces per 1,000 cubic feet. On the assumption just made c is in general $2.5/5.8 = 0.43$ C. Hence the above equation becomes, substituting for C'_0, its average value for this furnace,

$$C' = 0.098 + 0.57 k_2 C,$$

where k_2 represents the relation between the increase in per cent of alkali in the stock due to condensation from the gas and the corresponding decrease in the concentration of the alkali in the gas. As we have seen, about 35,000 cubic feet of gas passes upward past plane 4 each minute. In the same time about 1,297 pounds of stock moves downward, and this stock carries all of the alkali that condenses from the gas. The value of k_2 is therefore

$$\frac{35}{16 \times 1297} \times 100 = 0.169$$

when C′ is expressed as per cent of alkali (calculated as KCN) and C in ounces of alkali (calculated as KCN) per 1,000 cubic feet. Hence from the above equation,

$$C' = 0.98 + 0.57 \times 0.169C = 0.98 + 0.096C$$

when no gas is withdrawn. If a fraction, A, of the gas is withdrawn, then

$$C' = 0.98 + 0.096(1 - A)C.$$

By substituting this value of C′, in equation (5), it is seen that

$$C = kC' = k(0.98 + 0.096(1 - A)C). \tag{6}$$

When C and A are known k may be evaluated. At plane 4 C is 5.83 ounces per 1,000 cubic feet when A is zero. The value for k is found to be 3.78. Solving equation (6), we find then that the concentration of total alkali (calculated as KCN) to be expected when a fraction A of the gas is withdrawn continuously from a point where the concentration is 5.83 ounces per 1,000 cubic feet with no withdrawal, is expressed by the equation

$$C = \frac{3.71}{1 - 0.363\,(1 - A)}. \tag{7}$$

Table 19 gives the values of C, calculated by equation (7), when different fractions of gas are withdrawn, and shows also the fraction of the total alkali entering the furnace which would be drawn out with the gas.

TABLE 19.—*Calculated concentration of total alkali in the gases when fraction A is continuously withdrawn*

[Concentration with no withdrawal, 5.83 ounces per 1,000 cubic feet]

A, fraction of gases withdrawn	C, concentration of alkali, calculated as KCN, ounces per 1,000 cubic feet	Fraction of total alkali of charge withdrawn
0	5.83	0
0.1	5.51	0.10
.2	5.22	.19
.3	4.97	.27
.4	4.74	.34
.5	4.53	.41
0.6	4.34	0.47
.7	4.16	.53
.8	4.00	.58
.9	3.85	.63
1.0	3.71	.67

These calculations indicate that the concentration of alkali in the gas would not be greatly lowered by the withdrawal of a substantial fraction of the total gas. On the basis of these calculations the probable value of the cyanides recoverable at this furnace is estimated below.

ESTIMATE OF VALUE OF ALKALI CYANIDES THAT MIGHT BE RECOVERED

It might be possible, as already indicated, to withdraw as much as 40 per cent of the total gas at plane 4 without interfering with reduction in the shaft. In order to be conservative, however, let us first assume that only one-tenth of the total gas is withdrawn at this plane. According to the above calculation the alkali concentration in the gas under such conditions will be 5.51 ounces per 1,000 cubic feet. An average of about 60 per cent of this alkali will be combined as cyanide, making the cyanide content equivalent to 3.3 ounces of KCN per 1,000 cubic feet. The total daily production of cyanide if all of the gas were drawn off would be 10,400 pounds of KCN. In a comparatively pure state this cyanide should be worth about 15 cents per pound (corresponding, on the basis of equivalent CN content, to 20 cents per pound for NaCN) as a substitute for sodium cyanide now largely used. In the absence of data on the cost of recovery and purification, it will be assumed that the value of KCN in the crude fume at the plant is 10 cents per pound. On this basis the value of the daily recovery from one-tenth of the gas at plane 4 would be $104. In the same way it may be shown that, if the concentrations are as above calculated, when larger portions of gas are withdrawn the value of the cyanide recoverable in one day, provided that the larger amounts could be recovered successfully, would be $197 when 0.2, $282 when 0.3, and $358 when 0.4 of the total gas is withdrawn.

In this estimate of the value of the furnace fume recoverable the cyanides alone have been considered and no account has been taken of the potash. The suggestion is made that crude potassium salt could be obtained as a separate by-product by expelling HCN with a cheap acid, such as CO_2, and then either condensing the HCN to a liquid or absorbing it by a base cheaper than potash. The value of the potash salt so obtained would probably be of the order of one-third that calculated for the cyanide content of the fume.

There being, as already pointed out, no assurance that the point of maximum cyanide concentration was found, it is of interest to consider briefly how the recovery should be effected if a region of considerably higher concentration could be found. Assume that a point is found where the concentration of alkali compounds (60 per cent of the alkali being combined as cyanide) is 20 ounces (calculated as KCN) per 1,000 cubic feet. Then, by equation (6), the withdrawal of one-tenth of the total gas would lower the alkali concentration to 16.5 ounces per 1,000 cubic feet, 30 per cent of the total alkali charged would be recovered, and the value of the cyanide recovered would be $310 a day. If 30 per cent of the total gas could be withdrawn the concentration of alkali compounds would drop to 12.5 ounces per 1,000 cubic feet, 68 per cent of the total alkali charged would be recovered, and the value of the cyanide recovered would be $710 a day.

The reader should note that the assumption that 40 per cent of the gases may be removed has been made by the writers simply as a basis of calculation. It is quite possible that this amount of gas might be removed where conditions of operation are the best. It is believed that at least 10 per cent of the gases could be removed from the upper part of the bosh of any furnace with little effect on operation.

SUMMARY AND CONCLUSIONS

1. Previous work on the occurrence of alkali cyanides in the iron blast furnace is summarized.

2. A method for determining the alkali cyanide content of gases at different points in the interior of the blast furnace has been developed and the values for one furnace have been determined.

3. In the plane of the tuyères and also in a plane 27 inches above the tuyères the concentration of cyanides ranges from virtually nothing at the wall to about 3 or 4 ounces per 1,000 cubic feet at the center of the furnace. In a plane 19¼ feet above the tuyères (at the base of the shaft) the content is about 3 ounces per 1,000 cubic feet. This figure was confirmed by large-scale collection, in which cyanide was removed from about 0.5 per cent of the total gas for a short time.

4. The concentration of alkali cyanide in the fume from the slag notch varied widely, but was usually of the order of 10 to 20 ounces of KCN per 1,000 cubic feet.

5. Analyses of samples of blast-furnace fume collected at the plane 19¼ feet above the tuyères and at the slag notch are given.

6. Calculations made indicate that the concentration of alkali cyanide would not be greatly lowered by withdrawing a part of the gas for the recovery of cyanides.

7. It seems unlikely that the operation of the blast furnace would be adversely affected by the withdrawal of a small part of the gas for the recovery of cyanides. The amount of alkali cyanide recoverable in this way would be commercially significant.

8. If one-tenth of the gas at plane 4 be withdrawn it is estimated that the daily recovery of crude cyanide would be 1,040 pounds, which, at 10 a pound, would be worth $104.